

# Spin Fluctuation-Induced Superconductivity in Organic Compounds

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Spin fluctuation-induced superconductivity in two-dimensional organic compounds such as  $\kappa$ -(ET)<sub>2</sub>X is investigated by using a simplified dimer Hubbard model with right-angled isosceles triangular lattice (transfer matrices  $-\tau$ ,  $-\tau'$ ). The dynamical susceptibility and the self-energy are calculated self-consistently within the fluctuation exchange approximation and the value for  $T_c$  as obtained by solving the linearized Eliashberg-type equations is in good agreement with experiment. The pairing symmetry is of  $d_{x^2-y^2}$  type. The calculated  $(U/\tau)$ -dependence of  $T_c$  compares qualitatively well with the observed pressure dependence of  $T_c$ . Varying the value for  $\tau'/\tau$  from 0 to 1 we interpolate between the square lattice and the regular triangular lattice and find firstly that values of  $T_c$  for  $\kappa$ -(ET)<sub>2</sub>X and cuprates scale well and secondly that  $T_c$  tends to decrease with increasing  $\tau'/\tau$  and no superconductivity is found for  $\tau'/\tau = 1$ , the regular triangular lattice.

**KEYWORDS:** organic superconductor, spin fluctuation, Hubbard model, triangular lattice

Major topics in condensed matter physics in recent years may certainly include the unconventional superconductivity observed in high- $T_c$  cuprates, heavy electron systems and organic compounds. Among various possible mechanisms proposed so far the spin fluctuation mechanism seems to have possibilities of explaining all of these three.<sup>1)</sup> The superconductivity in heavy electron systems is believed to be almost certainly due to the spin fluctuation mechanism. Although the mechanism for cuprates is still controversial, the spin fluctuation mechanism seems to be rather unique in its ability of explaining not only the values of  $T_c$  and the pairing symmetry but also various anomalous physical properties in the normal state as well as in the superconducting state in a systematic fashion at least in the optimal and overdoped concentration regimes;<sup>2)</sup> the underdoped regime still remains to be clarified.

As for the two-dimensional (2D) organic superconductors the spin fluctuation mechanism seems to be the only available mechanism provided the superconducting order parameter is anisotropic, say of d-wave, as was indicated by recent investigations.<sup>3, 4, 5)</sup> Major differences of this problem from that of high- $T_c$  cuprates are that the superconductivity occurs without doping and in many cases in the metallic side of a metal-insulator Mott transition and thus the system should be in the intermediate correlation regime. For example, the  $t$ - $J$  model should safely be excluded.

We wish to discuss the spin fluctuation mechanism of superconductivity in 2D organic compounds, keeping  $\kappa$ -(ET)<sub>2</sub>X [ET = BEDT-TTF, X = Cu{N(CN)<sub>2</sub>}X', X' = Cl, Br] in mind.<sup>6)</sup> According to experiment  $\kappa$ -(ET)<sub>2</sub>X [X' = Cl] is an antiferromagnetic insulator and under increasing pressure it undergoes a insulator to superconductor transition.<sup>7)</sup> Each layer of molecules in these

compounds may be regarded as consisting of dimers each of which has one hole in the antibonding dimer orbital of the highest occupied molecular orbitals (HOMO).<sup>8, 9)</sup> There are transfer matrices  $-\tau$  ( $\tau > 0$ ) between dimers and the additional consideration of intra-dimer electron interaction  $U$  naturally leads to the Hubbard model. For  $U \gg \tau$  we have antiferromagnetic ground state and with decreasing  $U/\tau$  we encounter an insulator to metal Mott transition at a certain value of  $U/\tau$ .

We now wish to study possible superconductivity on the metallic side of this transition. For this purpose we make use of a half-filled single band Hubbard model consisting of antibonding dimer orbitals with the inter-dimer transfers and the intra-dimer electron interaction. The spin fluctuations are treated within the renormalized random phase approximation (RRPA) or the fluctuation exchange (FLEX) approximation.<sup>10)</sup> Although the formalism of the self-consistent renormalization (SCR) theory takes into account the vertex corrections,<sup>11)</sup> associated numerical jobs seem to be too heavy to carry them through. The results of FLEX for cuprates so far seem to be fairly successful and there are a few arguments on vertex corrections in support of the FLEX approach.<sup>2, 12, 13, 14, 15, 16, 17)</sup>

Thus we see that the problem itself is reduced to the one quite similar to the Hubbard model description of cuprates. Only difference is the lattice structure and the transfer matrices. As a matter of fact we may simplify, to a good approximation, the model for  $\kappa$ -(ET)<sub>2</sub>X to a square lattice with the nearest neighbor transfers  $\tau$  and one of the cross diagonal second neighbor transfers  $\tau'$  (say up right corner to down left), thus making a right-angled isosceles triangular lattice with transfer matrices  $-\tau$  for the two sides and  $-\tau'$  for the base, Fig. 1(a).<sup>18)</sup> The value for  $\tau'/\tau$  as estimated from the presently ac-

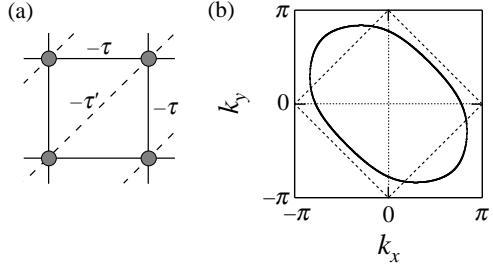


Fig. 1. (a) The model unit cell and the transfer integrals. (b) Unperturbed Fermi surface for  $\tau'/\tau = 0.8$ . Dashed lines show the antiferromagnetic zone boundary.

cepted values for the transfer integrals is about 0.8 (close to 1) for  $\kappa$ -(ET)<sub>2</sub>X.<sup>8,9)</sup> This reminds us of the magnetic frustration problem in an equilateral triangular lattice. So we study not only the case of  $\kappa$ -(ET)<sub>2</sub>X but also the problem for varying values of  $\tau'/\tau$ , including the regular triangle:  $\tau'/\tau = 1$ .

The model Hamiltonian is given by

$$H = - \sum_{\sigma} \sum_{\langle i,j \rangle} \tau a_{i\sigma}^{\dagger} a_{j\sigma} - \sum_{\sigma} \sum_{(i,j)} \tau' a_{i\sigma}^{\dagger} a_{j\sigma} + U \sum_j n_{j\uparrow} n_{j\downarrow} \quad (1)$$

$$= - \sum_{\sigma} \sum_{\mathbf{k}} \epsilon_{\mathbf{k}} a_{\mathbf{k}\sigma}^{\dagger} a_{\mathbf{k}\sigma} + U \sum_j n_{j\uparrow} n_{j\downarrow}, \quad (2)$$

with

$$\epsilon_{\mathbf{k}} = -2\tau (\cos k_x a + \cos k_y a) - 2\tau' \cos (k_x a + k_y a), \quad (3)$$

where  $\langle i,j \rangle$  and  $(i,j)$  indicate the nearest neighbor pairs and the second neighbor side diagonal pairs, respectively, as shown in Fig. 1(a) and  $a$  is the lattice constant.

The equations for the normal and anomalous Green's functions are given by

$$G(\mathbf{k}, i\omega_n) = G^{(0)}(\mathbf{k}, i\omega_n) + G^{(0)}(\mathbf{k}, i\omega_n) \left[ \Sigma^{(1)}(\mathbf{k}, i\omega_n) G(\mathbf{k}, i\omega_n) - \Sigma^{(2)}(\mathbf{k}, i\omega_n) F^*(\mathbf{k}, i\omega_n) \right], \quad (4)$$

$$F^*(\mathbf{k}, i\omega_n) = G^{(0)}(-\mathbf{k}, -i\omega_n) \times \left[ \Sigma^{(1)}(-\mathbf{k}, -i\omega_n) F^*(\mathbf{k}, i\omega_n) + \Sigma^{(2)}(-\mathbf{k}, -i\omega_n) G(\mathbf{k}, i\omega_n) \right], \quad (5)$$

where  $G^{(0)}(\mathbf{k}, i\omega_n)$  is the Green's function for a non-interacting system and the self-energies due to the spin and charge fluctuations are given as follows:

$$\Sigma^{(1)}(\mathbf{k}, i\omega_n) = \frac{T}{N_0} \sum_{\mathbf{q}, m} V^{(1)}(\mathbf{q}, i\Omega_m) \times G(\mathbf{k} - \mathbf{q}, i\omega_n - i\Omega_m), \quad (6)$$

$$\Sigma^{(2)}(\mathbf{k}, i\omega_n) = -\frac{T}{N_0} \sum_{\mathbf{q}, m} V^{(2)}(\mathbf{q}, i\Omega_m) \times F^{(2)}(\mathbf{k} - \mathbf{q}, i\omega_n - i\Omega_m), \quad (7)$$

with

$$V^{(1)}(\mathbf{q}, i\Omega_m) = U + U^2 \left[ \frac{3}{2} \chi_s(\mathbf{q}, i\Omega_m) + \frac{1}{2} \chi_c(\mathbf{q}, i\Omega_m) - \frac{1}{2} \{ \bar{\chi}_s(\mathbf{q}, i\Omega_m) + \bar{\chi}_c(\mathbf{q}, i\Omega_m) \} \right], \quad (8)$$

$$V^{(2)}(\mathbf{q}, i\Omega_m) = U + U^2 \left[ \frac{3}{2} \chi_s(\mathbf{q}, i\Omega_m) - \frac{1}{2} \chi_c(\mathbf{q}, i\Omega_m) - \frac{1}{2} \{ \bar{\chi}_s(\mathbf{q}, i\Omega_m) - \bar{\chi}_c(\mathbf{q}, i\Omega_m) \} \right], \quad (9)$$

and

$$\chi_s(\mathbf{q}, i\Omega_m) = \frac{\bar{\chi}_s(\mathbf{q}, i\Omega_m)}{1 - U \bar{\chi}_s(\mathbf{q}, i\Omega_m)}, \quad (10)$$

$$\chi_c(\mathbf{q}, i\Omega_m) = \frac{\bar{\chi}_c(\mathbf{q}, i\Omega_m)}{1 + U \bar{\chi}_c(\mathbf{q}, i\Omega_m)},$$

$$\bar{\chi}_s(\mathbf{q}, i\Omega_m) = -\frac{T}{N_0} \sum_{\mathbf{k}, n} [G(\mathbf{k} + \mathbf{q}, i\omega_n + i\Omega_m) G(\mathbf{k}, i\omega_n) + F(\mathbf{k} + \mathbf{q}, i\omega_n + i\Omega_m) F(\mathbf{k}, i\omega_n)], \quad (11)$$

$$\bar{\chi}_c(\mathbf{q}, i\Omega_m) = -\frac{T}{N_0} \sum_{\mathbf{k}, n} [G(\mathbf{k} + \mathbf{q}, i\omega_n + i\Omega_m) G(\mathbf{k}, i\omega_n) - F(\mathbf{k} + \mathbf{q}, i\omega_n + i\Omega_m) F(\mathbf{k}, i\omega_n)], \quad (12)$$

where  $\omega_n = (2n + 1)\pi T$  and  $\Omega_m = 2m\pi T$  are the Fermi and the Bose Matsubara frequencies, respectively and  $N_0$  is the number of dimers in the crystal. We study have the possibility of singlet pairing.

Confining ourselves here to the transition temperature  $T_c$  and the normal state properties we may linearize the equations (4, 5) and (11, 12) with respect to the anomalous self-energy  $\Sigma^{(2)}(\mathbf{k}, i\omega_n)$  or  $F^{(2)}(\mathbf{k}, i\omega_n)$ .  $T_c$  can be calculated as the highest temperature where the following equation for the normalized anomalous self-energy  $f(\mathbf{k}, i\omega_n) = \Sigma^{(2)}(\mathbf{k}, i\omega_n) |G(\mathbf{k}, i\omega_n)|$  has a non-trivial solution:

$$f(\mathbf{k}, i\omega_n) = -\frac{TU}{N_0} \sum_{\mathbf{p}, m} |G(\mathbf{k}, i\omega_n)| \left[ 1 + \frac{3}{2} U \chi_s(\mathbf{k} - \mathbf{p}, i\omega_n - i\omega_m) - \frac{1}{2} U \chi_c(\mathbf{k} - \mathbf{p}, i\omega_n - i\omega_m) \right] \times |G(\mathbf{p}, i\omega_m)| f(\mathbf{p}, i\omega_m). \quad (13)$$

The symmetry of the order parameter is given by that of  $f(\mathbf{k}, i\omega_n)$ . Since the kernel of eq. (13) has a full symmetry of the model Hamiltonian we may classify the order parameter according to the irreducible representations of the symmetry group. There are four one-dimensional irreducible representations  $A_1$ ,  $A_2$ ,  $B_1$  and  $B_2$ . We take

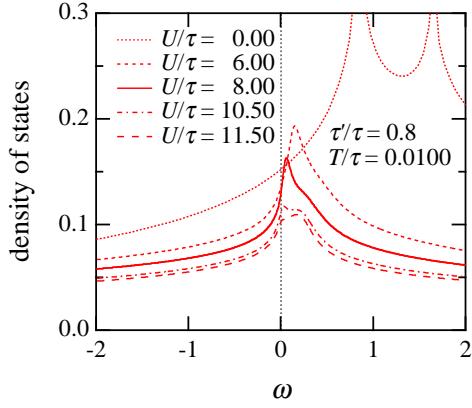
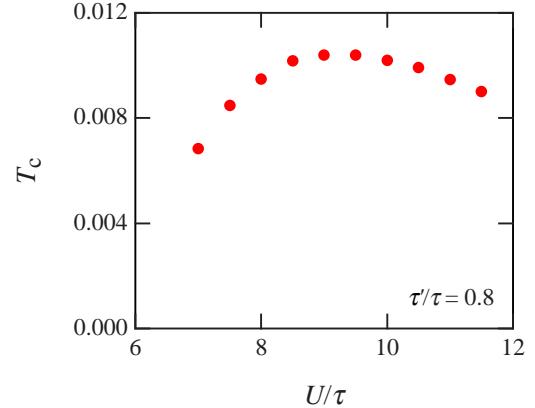
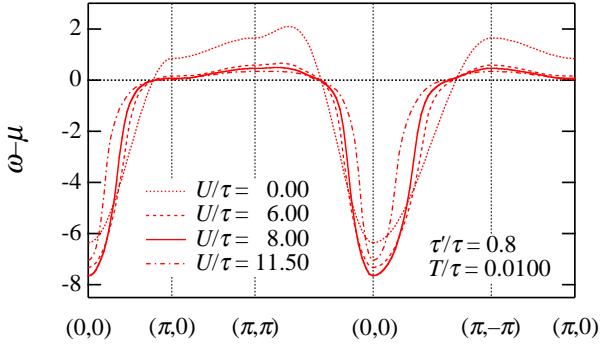
Fig. 2. Density of states for various values of  $U/\tau$ .Fig. 5.  $T_c$  vs.  $U/\tau$ .

Fig. 3. Quasi-particle dispersion.

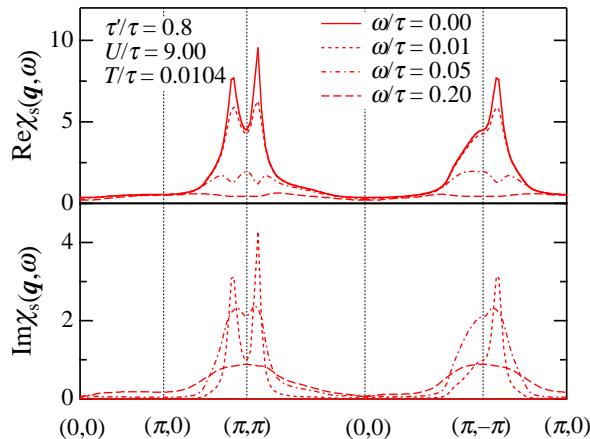


Fig. 4. Dynamical susceptibility.

advantage of using this symmetry property in the calculation.<sup>19)</sup> For numerical calculations we take  $64 \times 64$   $\mathbf{k}$ -points and 512 and 2048 Matsubara frequencies for susceptibility and self-energy, respectively.

We first show the results of calculation for  $\kappa$ -(ET)<sub>2</sub>X ( $\tau'/\tau = 0.8$ ). The unperturbed Fermi surface is shown in Fig. 1(b). The one particle density of states and the quasi-particle dispersions are shown in Figs. 2 and

3, respectively, together with the corresponding values for  $U = 0$ . The dynamical susceptibilities are shown in Fig. 4 for various frequencies. We see that incommensurate peaks around  $(\pi, \pi)$  and an asymmetric peak around  $(\pi, -\pi)$  are strongly enhanced.

The superconducting transition temperature  $T_c$  is given as  $T_c = 0.0105\tau$  for  $U = 9\tau$  and the order parameter has the  $A_2$  symmetry ( $x^2 - y^2$ ). Estimating  $\tau \sim 0.07\text{eV}$ , we get  $T_c \sim 9\text{K}$  in fair agreement with the observed value  $T_c \sim 10\text{K}$ . Fig. 5 shows the plot of  $T_c$  vs.  $U/\tau$ .  $T_c$  shows a weak maximum at  $U/\tau \sim 9$  and then decreases with decreasing  $U/\tau$ . Since  $U/\tau$  should decrease with increasing pressure, this tendency is consistent with the observed pressure dependence of  $T_c$  if we assume a proper critical value  $(U/\tau)_c$ , say around 10, for the insulator-superconductor transition.<sup>7, 20)</sup> According to the mean field calculation, which normally underestimate the critical point for transition, the first order transition between the insulator and metallic phases takes place at  $U/\tau = 4.2$ .<sup>9)</sup> It still remains to calculate the critical value  $(U/\tau)_c$  by using the same FLEX approximation for both antiferromagnetic and superconducting states at  $T = 0$ .

We also note that the calculated values of  $T_c$  for  $\kappa$ -(ET)<sub>2</sub>X and cuprates properly scale. A crude model for some of the cuprates, say LSCO, may correspond to the case of  $\tau'/\tau \approx 0$  with less than half-filled carriers. According to the previous calculations we have  $T_c/\tau = 0.0273$  (0.021) for  $\tau'/\tau = 0$  (0.15 for cross diagonal transfers),  $U/\tau = 6$  (4) and the carrier number  $n = 0.875$ .<sup>12, 13)</sup> Since the band width of cuprates is considered to be roughly  $2 \sim 4$  times larger than that in  $\kappa$ -(ET)<sub>2</sub>X, the calculated relative values of  $T_c$  compare rather well with experiment.

Next we discuss the  $(\tau'/\tau)$ -dependence of  $T_c$  for the half-filled case. It is interesting to find that eq. (13) has no solution for  $\tau'/\tau = 1$  (the regular triangular lattice) in any reasonable range of the value for  $U/\tau$ , or  $U/\tau < 16$ , the highest value studied. For  $U/\tau \gg 1$  and  $\tau'/\tau = 1$  we have an antiferromagnetic Heisenberg model with a regular triangular lattice, a famous frustrated sys-

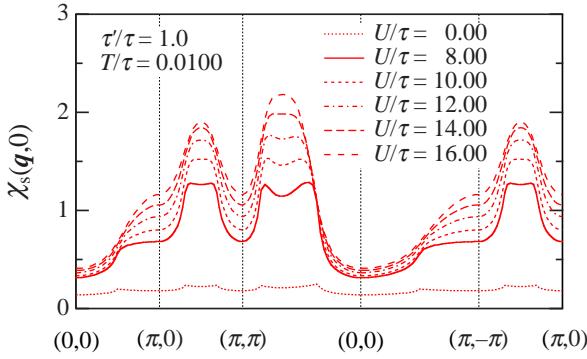


Fig. 6. Wave vector dependence of the susceptibility for  $\tau'/\tau = 1.0$ , the regular triangular lattice, for various values of  $U/\tau$ .

tem.<sup>21)</sup> Around the Mott transition under pressure the local moments disappear and the metallic phase seems to be characterized by a wave vector dependent magnetic susceptibility with three broad peaks as is shown in Fig. 6. This situation does not seem favorable for the spin fluctuation-induced superconductivity as may be seen from a weak coupling argument.<sup>22)</sup>

In the case of  $\tau'/\tau = 0.4$ , the antiferromagnetic peak of the dynamical susceptibility is more significant than for  $\tau'/\tau = 0.8$  and the superconductivity appears for smaller  $U$  and the value of  $T_c$  is higher as may naturally be expected. For example, we have  $T_c/\tau = 0.014$  and 0.016 for  $U/\tau = 3.3$  and 3.7, respectively. For a half-filled band we may conjecture as follows: Considering a phase diagram in  $U/\tau$  vs.  $\tau'/\tau$  plane, the critical boundary for antiferromagnetism  $(U/\tau)_{\text{AF}}$  is lower than that for superconductivity  $(U/\tau)_{\text{SC}}$  for small values of  $\tau'/\tau$  where the nesting condition is well satisfied. With increasing  $\tau'/\tau$  the frustration increases and its destructive influence is stronger for antiferromagnetism than for superconductivity and thus  $(U/\tau)_{\text{SC}}$  becomes lower than  $(U/\tau)_{\text{AF}}$  beyond a certain value of  $\tau'/\tau$ . For a definite conclusion it is necessary to compare the free energies of both of these states.

As for the normal state properties the uniform susceptibility is almost constant and has weak tendency of decreasing with decreasing temperature. The calculated values for  $\sum_{\mathbf{q}} \text{Im}\chi(\mathbf{q}, \omega)/\omega$ , the quantity proportional to  $1/T_1 T$ ,  $T_1$  being the nuclear spin-lattice relaxation rate, has a Curie-Weiss like temperature dependence down to  $T_c$ . On the other hand the experimental results on  $\kappa\text{-}(\text{ET})_2X$  [ $X' = \text{Br}$ ] show a substantial decrease of the susceptibility as  $T_c$  is approached and the peak structure of  $1/T_1 T$  much above  $T_c$ .<sup>3,4,5)</sup> These behaviors remain to be explained.

In summary we have studied the spin fluctuation mechanism of superconductivity in  $\kappa\text{-}(\text{ET})_2X$  by using a FLEX approximation for a dimer Hubbard model with the effective transfer integrals  $-\tau$ ,  $-\tau'$  deduced from the presently accepted values for the transfer integrals and varying values of  $U$ . We found superconductivity of  $d_{x^2-y^2}$  types. The value for  $T_c$  and its  $U/\tau$  (pres-

sure) dependence compare well with experiments. We point out that if we vary the value of  $\tau'/\tau$  in the present model for  $\kappa\text{-}(\text{ET})_2X$  between 0 and 1 the square lattice and the regular triangular lattice Hubbard models are interpolated. We find that the values of  $T_c$  for  $\kappa\text{-}(\text{ET})_2X$  and for cuprates scale fairly well and there is no superconductivity of singlet pairing for the triangular lattice within a reasonable range of the value for  $U$ . However, the anomalous normal state properties in the uniform susceptibility and the nuclear spin-lattice relaxation rate, bearing resemblance to the pseudo-spincgap phenomena in cuprates, remain to be explained. Also, the transition between the antiferromagnetic insulator and superconducting phases is still to be investigated.

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